Charcoal and stable soil organic matter as indicators of fire frequency, climate and past vegetation in volcanic soils of Mt. Etna, Sicily

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Abstract: Charcoal fragments in soils are useful to reconstruct past vegetation because the level of preservation is often good enough to determine the tree genus. All forest ecosystems have the potential to burn as a result of naturally occurring or human-induced fires. Forest fires are coupled to climate and are a not-negligible factor of pedogenesis in Mediterranean areas, where they occur frequently. Furthermore, soil organic matter (SOM) is prone to undergo peculiar changes due to forest fires, both in terms of quantity and quality. A soil sequence along an elevational gradient ranging from Mediterranean to subalpine climate zones on slopes of Mt. Etna (Sicily, Italy) was investigated in respect of soil organic C and charcoal. The amount of charcoal and the identification of charred species gave an indication of the fire frequency and vegetation changes that have occurred in the past. The distribution into labile and stable organic fractions provided insight into the stabilisation and turnover mechanisms of SOM. The stable organic matter fraction was measured as the residue of a H2O2 treatment. The soils along the altitudinal sequence are variations of Vitric Andosols that developed on a single trachy-basaltic lava flow having an age of 10–15 ky BP. Maquis vegetation dominates at the lower sites of the toposequence, followed by oak- and chestnut-forests at mid elevations, and pine-forest at the highest-elevated sites. Charcoals are older at higher elevations (ages of up to 1.5 ky cal BP). Here, the vegetation type has not changed over the last > 1000 years, as all charcoal pieces were identified as Pinus nigra. Charred material at the lower sites could be identified as particles of deciduous shrubs, Quercus, Castanea sativa, Lonicera implexa and Cytisus spp. with mostly a modern age up to about 300 y cal BP. A similar finding was obtained for the stable (H2O2 resistant) SOM. Very high ages for this fraction were found at the highest elevations where it had an age of up to 8.2 ky BP — an age that is close to the start of soil formation. At the lower sites, where frequent bush fires often destroyed a part of the stable fraction, the stable SOM fraction had a maximum age of 1 ky. The studied soils have recorded the signals of the interrelated factors fire frequency, climatic effects and vegetation whose role cannot always be clearly distinguished. With decreasing altitude and with a warmer climate, vegetation changes and fire frequency, org. C and especially nitrogen abundance and the amount of labile SOM increases. At the lower sites, charcoal particles reflect the more recent vegetation probably because the repeated fires here hindered their preservation. Our findings hence suggest that a high fire frequency is a powerful rejuvenating factor for soil organic matter, removing part of the old SOM and promoting plant recolonisation that is a source of young SOM. Fire frequency and intensity on Mt. Etna is, however, moderate enough even at the lowest altitudes for the organic matter pool to be high and not depleted.

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Charcoal and stable soil organic matter as indicators of fire frequency, climate and past vegetation in volcanic soils of Mt. Etna, Sicily

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Abstract

Charcoal fragments in soils are useful to reconstruct past vegetation because the level of preservation is often good enough to determine the tree genus. All forest ecosystems have the potential to burn as a result of naturally-occurring or human-induced fires. Forest fires are coupled to climate and are a not-negligible factor of pedogenesis in Mediterranean areas, where they occur frequently. Furthermore, soil organic matter (SOM) is prone to undergo peculiar changes due to forest fires, both in terms of quantity and quality. A soil sequence along an elevational gradient ranging from Mediterranean to subalpine climate zones on slopes of Mt. Etna (Sicily, Italy) was investigated in respect of soil organic C and charcoal. The amount of charcoal and the identification of charred species gave an indication of the fire frequency and vegetation changes that have occurred in the past. The distribution into labile and stable organic fractions provided insight into the stabilisation and turnover mechanisms of SOM. The stable organic matter fraction was measured as the residue of a H_2O_2 treatment. The soils along the altitudinal sequence are variations of Vitric Andosols that developed on a single trachy-basaltic lava flow having an age of 10 – 15 kyBP. Maquis vegetation dominates at the lower sites of the toposequence, followed by oak- and chestnut-forests at mid elevations, and pine-forest at the highest-elevated sites. Charcoals are older at higher elevations (ages of up to 1.5 ky calBP). Here, the vegetation type has not changed over the last > 1000 years, as all charcoal pieces were identified as *Pinus nigra*. Charred material at the lower sites could be identified as particles of deciduous shrubs, *Quercus, Castanea sativa*, *Lonicera implexa* and *Cytisus* spp. with mostly a modern age up to about 300 y calBP. A similar finding was obtained for the stable (H_2O_2 resistant) SOM. Very high ages for this fraction were found at the highest elevations where it had an age of up to 8.2 kyBP – an age that is close to the start of soil formation. At the lower sites, where frequent bush fires often destroyed a part of the stable fraction, the stable SOM fraction had a maximum age of 1 ky. The studied soils have recorded the signals of the interrelated factors fire frequency, climatic effects and vegetation whose role cannot always be clearly distinguished. With decreasing altitude and with a warmer climate, vegetation changes and fire frequency, org. C and especially nitrogen abundance and the amount of labile SOM increases. At the lower sites, charcoal particles reflect the more recent vegetation probably because the repeated fires here hindered their preservation. Our findings hence suggest that a high fire

frequency is a powerful rejuvenating factor for soil organic matter, removing part of the old SOM and promoting plant recolonisation that is a source of young SOM. Fire frequency and intensity on Mt. Etna is, however, moderate enough even at the lowest altitudes for the organic matter pool to be high and not depleted.

Keywords: charcoal, 14C dating, climate, stable soil organic matter, Mediterranean, volcanic soils

Introduction

Earth is an intrinsically flammable planet owing to its cover of carbon-rich vegetation, atmospheric oxygen, seasonally dry climates and widespread lightning and volcanic ignitions (Bowman et al., 2009). Due to global warming, the temperature increase will be pronounced in Central Europe and the Mediterranean areas where, due to the projected decrease in precipitation, dramatic environmental changes must be expected (Moriondo et al., 2006; IPCC Fourth Assessment Report, 2007; Bates et al., 2008). The Mediterranean climate is characterised by a strong seasonal winter/summer rainfall contrast with the result that the soils and the root zone are dry during the summer, often for several months. The long dry summer period facilitates the occurrence of bush and tree fires, which exert a significant effect on landscape evolution (Naveh, 1990; Shakesby, 2011). Fire has a strong influence on vegetation composition, structure and distribution at both a local and global scale. The general pattern of fire periodicity, seasonality, intensity, duration and size that emerges in any landscape over time comprises the fire regime for that environment and has important consequences for vegetation development. Understanding the fire regime of an area is crucial for fire management purposes and for research concerned with the ecological role of fire (Whelan, 1995). Up to now, the relation between the vegetation type and fire regime has only rarely been investigated in palaeorecords (charcoal, pollen, lake sediments) of the Mediterranean basin (e.g. Sadori et al., 2008). Whether natural or human-induced, fire serves as a regular ecosystem process, influencing vegetation patterns, wildlife distribution, nutrient cycling and many other ecosystem elements (Moody et al., 2006).

Changes in climate and vegetation type are expected to alter the quality and quantity of detritus inputs to soil and also the soil chemical, microbiological and physical processes that regulate the quality of soil organic matter (SOM). The SOM abundance is the product of a dynamic equilibrium between gain and losses. Several investigations have clearly shown that SOM and other soil properties can be influenced by climate (carbon stocks, organic matter chemistry, morphology and functional characters of humus forms) and may quickly react to changing environmental conditions (e.g. Laffan et al., 1989; Bäumler and Zech, 1994; Bockheim et al., 2000; Zanelli et al., 2006). In turn, changes in the quality and quantity of SOM can affect soil chemistry and mineralogy. However, despite advances in our understanding of the specific mechanisms leading to SOM formation and stabilisation, there is a surprisingly poor understanding of how soil quality (including the mineral and organic part) relates to climate and vegetation factors. This knowledge gap compromises our ability to predict the response of SOM storage and several other properties of soils to global change because positive effects of warming on SOM quality could result in a positive feedback on future warming; conversely, warming-related reductions in SOM quality could result in negative feedback.

The effect of fire can be recognised via structural characteristics of soil organic matter (Tinoco et al., 2006) or on the SOM accumulation. On the one hand, fire can cause a substantial loss of SOM in soils (Novara et al., 2010; Certini et al., 2011) that may also be made greater due to the subsequent increased erosion effect after a bush fire. On the other hand, a substantial input of charcoal and charred organic matter (black carbon) that are due to fire activities (aboveground biomass) may lead to increased SOM stocks in soils (Eckmeier et al., 2010). Already Schmidt et al. (1999) suggested that burning vegetation produces large amounts of highly refractory organic matter consisting of charcoal and partially charred plant material that can have a major impact on composition, turnover and formation of soil organic matter. Both climate and fire affect the SOM properties and stocks. It is often very difficult to isolate one factors from the other. Furthermore, the climate effect is partially overshadowed because it also influences the state factor vegetation (although this factor is not really fully independent – according to the paradigm of Jenny (1941)). The Mediterranean area is an interesting region in which to study the effect of fire and climate on SOM fractions. Here, we investigated a soil climosequence along the slopes of Mt. Etna (Sicily), the largest volcano in Europe. A strong effect of the altitude on pedogenesis on the flanks of the volcano was assessed, even when covered by the same vegetation (Fernández Sanjurjo et al., 2003). We hypothesised that fire activity effects pedogenesis because it is higher at the lower sites (see Egli et al., 2007). This is assumed to affect the SOM characteristics and also the corresponding stocks. It is not yet known what effect the fire frequency has had on the different fractions and nature of SOM in these soils and on the turnover rates of stable and less stable fractions. We therefore performed physical, chemical and isotopic analyses on soils taken from of an altitudinal-vegetational gradient of the volcano. Furthermore, the use of a powerful tool — the analysis (extraction, identification and radiocarbon dating) of macrofossil charcoal fragments buried in soils (Carcaillet and Brun, 2000; Favilli et al., 2010) — allowed us to reconstruct fire activities, vegetation and climate. Through this analysis, a further valuable insight into climate and fire effects on landscape evolution and SOM quantity and quality of Mt. Etna is expected.

Investigation area

The Etna volcano was formed at the beginning of the Quaternary in the north-eastern part of Sicily (Branca et al., 2008) and is an isolated mountain region in southern Italy in the centre of the Mediterranean region (35° 50’ N/ 15° E) with an area of about 1570 km^2 (Poli Marchese, 2004) and a maximum altitude of 3323 m asl. The landscape is characterised by lava-flows of different ages and the most important geomorphological elements are the still active main and secondary craters. According to Poli Marchese (2004) the following vegetation zones can be defined in the Etna region:

a) basal-Mediterranean zone with a thermo-mediterranean subzone (Oleo-Ceratonion, below 500-600 m asl), a meso-Mediterranean subzone (Quercion ilicis; between 600 and 1100 m asl) and a supra-Mediterranean zone (Quercetalia pubescentis; between 1100 and 1500 m asl)
b) montane-Mediterranean zone between 1500 and 2400 m asl (with Fagetalia sylvaticae*, Astragaletum siculi, Pinus nigra* ssp.*, Laricio* (Querco-Fagetea), …)
c) Mediterranean high-alpine zone: above 2400 m asl (*Rumici Anthemidetum aetnensis*)

A regional nature park protects a substantial part of the area around the volcano (590 km^2). Human impact is, however, an important environmental factor in the Etna region. Large areas around the Etna volcano have been disturbed over centuries by human activity (agriculture). Undisturbed soils are usually found at high altitudes and on relatively young lava flows. Crops and various fruit orchards can be usually found up to c. 900 m asl (Dazzi, 2007). From 900 asl, forest vegetation prevails up to about 2200 m asl (the distribution and upper limit depend on the local exposure and morpho-climatic conditions). Also where anthropogenic intervention was restricted to forestation, the choice of the planted species influenced pedogenesis on weatherable substrata (Certini et al., 2001). A wide variation of soil types can be found that is due, among others, to the different ages, climatic features, topography or ash and lapilli input. According to the soil map (1:250000) of Sicily (Fierotti et al., 1988), Dazzi (2007) and Lulli (2007), mature and undisturbed soils of the Etna comprise Eutric or Dystric Cambisols and (Mollic) Andosols along the entire altitudinal sequence. Most of these soils have vitric charactertistics (Lulli, 2007; Dazzi, 2007).

Material and Methods

Sampling and sites

We investigated six sites along an elevational gradient ranging from Mediterranean (551 m asl; warm, semi-arid to sub-humid climate) to subalpine (1772 m asl; cold, humid climate) climate zones in the Etna region (Table 1, Fig. 1). Soil moisture and temperature regimes vary between xeric to udic and thermic to frigid (Raimondi et al., 1999). Five sites were located on one single lava flow and a sixth one on a separate flow (having the same characteristics). The lava flows were trachy-basalts (alkali mugearite) that could be attributed to the recent Mongibello chronozone (8ky) or the ancient Mongibello chronozone (about 15ky). Dating of lava flows in the Etna region was done by chronostratigraphic studies (Romano, 1979; 1983) and radiometric dating ($^{230}Th/^{238}U$ in Condomines et al., 1982; K-Ar in Gillot et al., 1994). All selected sites (soil profiles) were north-facing and the chemical and mineralogical composition of the parent material was identical (Nater, 2006). Two different types of vegetation can be distinguished along the elevational gradient. At the lower altitudes (4 sites between 551-1090 m asl), vegetation is dominated by maquis vegetation and oak/chestnut forests and at the higher altitudes (2 sites at 1515 and 1772 m asl, respectively) by coniferous forests (Corsican pine, *Pinus nigra Arn ssp. laricio*).

At each of these 6 sites, the following sampling procedure was applied:

- two soil profiles were sampled by horizons, down to the C or BC horizon (data of one soil profile was already available in Egli et al. (2007)).
- Another 2 – 3 to profiles (replicates) were sampled at 0 – 15 and 15 – 40 cm depth intervals.

With this procedure, a large amount of soil samples per site was collected that enable to cope with the spatial variability of soils (Hitz et al., 2002). From 1 to 3 kg soil material was sampled per soil horizon or soil depth. In fact, to yield reasonable results, unusually large sampling volumes are needed for soils on coarse textures (Hitz et al., 2002), such as those investigated. Soil bulk density was determined by a soil core sampler (100 cm^3, with 2 – 4 replicates per soil horizon) or by excavated holes backfilled with quartz sand. Taking advantage of the profile pits, undisturbed soil samples were taken down to the C horizon. The soils did not exhibit any signs of erosion or relocation and therefore they could be considered as natural and as relatively undisturbed.

Soil chemistry and physics

The soil samples were air-dried, large aggregates were gently crushed by hand and sieved to < 2 mm. Total C and N contents of the soil, soil fractions and charcoal pieces were measured using a C/H/N analyser (Elementar Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany) on oven-dried (70°C, 48h) and ball-milled material. Soil pH (in 0.01 M $CaCl_2$) was determined using a soil solution ratio of 1:2.5. The total elemental composition of the soil fine earth samples was analysed by X-ray fluorescence spectrometry (XRF). Around 6 g of fine earth material were milled to < 60 µm in a Retsch MM400 mill with Zr grinding tools. 4.0 g of the sample powder were mixed with 0.90 g of Licowax® C Micro-Powder PM (Fluxana, Germany), pressed into a 32 mm-pellet and analysed using an energy dispersive X-ray fluorescence spectrometer (SPECTRO XEPOS, SPECTRO Analytical Instruments, Germany).

After a pre-treatment with 3% H_2O_2, the particle size distribution of the soils was measured by a combined method consisting of sieving the coarser particles (2000 – 32 µm) and the measurement of the finer particles (< 32 µm) by means of an X-ray sedimentometer (SediGraph 5100, Micromeretics, Norcross, GA, USA).

The vitric content of the fine earth fraction was estimated in the field using a hand lens (0.1 mm scale graduated magnifying glass).

The exchangeable base cations and acidity were determined using the $BaCl_2$ method according to MIPAF (1999).

Soil organic matter fractionation

Assuming that chemical oxidation mimics natural oxidative processes, we treated the soils with 10% H_2O_2 to eliminate the more labile organic material from the more refractory organic matter (Plante et al., 2004; Eusterhues et al., 2005; Helfrich et al., 2007; Favilli et al., 2008). The fraction left at the end of the treatment usually represents very stable SOM (Favilli et al., 2009). Air-dried fine earth was wetted for 10 minutes with few ml of distilled water in a 250 ml glass beaker. Afterwards, 90 ml of 10% H_2O_2 per gram of soil were added. The procedure was run at a minimum temperature of 50 °C throughout the treatment period. To avoid evaporation of the reagent, the treatment was run in an automated, closed system using steel stirrers. Peroxide treatments were performed for 168 hours (7 days). At the end of the treatment the samples were washed three times with 40 ml of deionised water per gram of soil, freeze-dried, weighted and analysed for total C and N and ^{14}C-dated.

Charcoal

Charcoal fragments were separated from the soil material by hand-picking or floating and subsequently dried at 40 °C. The individual particles were analysed microscopically and separated into coniferous and broad-leaved tree species (Schoch, 1986) with a stereomicroscope (magnification 6.4 – 40x, Wild M3Z Leica, Germany). The charcoal fragments from the coniferous trees were further divided at the genus level using a reflected-light microscope (objective 5x, 10x, and 20x, Olympus BX 51, Japan). The observations were compared with a histological wood-anatomical atlas, using an identification key (Schweingruber, 1990). After the identification, some selected charcoal pieces were radiocarbon dated.

Radiocarbon dating

The CO_2 of the combusted samples (soil and charcoal samples) was catalytically reduced over iron powder at 550°C to elemental carbon (graphite). The obtained mixture was pressed into a target and the ratios ^{14}C:^{12}C (for radiocarbon age) were measured (including the $\partial^{13}C$) by Accelerator Mass Spectrometry (AMS) using the tandem accelerator of the Institute of Particle Physics at the Swiss Federal Institute of Technology Zürich (ETHZ). The calendar ages were calculated with the OxCal 4.1 calibration program (Bronk Ramsey 2001, 2009) based on the IntCal 04 calibration curve (Reimer et al., 2009). Calibrated ages are given in the 2 σ range (minimum and maximum value).

Statistics

The individual datasets were checked for normal distribution using a Shapiro-Wilk test (SigmaPlot 11.0). This test is robust also with a small number of observations (Jann, 2005). Depending on the data distribution (normal or not normal distribution), the Pearson product-moment or the Spearman rank correlation coefficient was used, respectively. This procedure was checked using a two-tailed test for significance.

Results

General soil properties

The top and subsoils in the study area usually had a sandy loam (Table 2) and in some cases a sandy silt loam or clay loam texture. The soil material contained a significant amount of glass particles (> 5%). Soil skeleton was in most cases between 10 and 30% by weight. Grain sizes usually decreased from the parent material to the surface soil horizon where the highest clay and silt contents were found. The general decrease of the grain sizes with depth is a concomitant effect of weathering (the physical breakdown of the coarse glass-particles and chemical-mineralogical transformations) and, presumably, of eolian ashy additions due to the eruptions of Etna.

Criteria for andic soil properties (Soil Survey Staff, 2010) were examined for the whole pedon. Soil density was generally too high to make it typically andic (< 0.90 g/cm^3, according to both, the World Reference Base for Soil Resources (IUSS Working Group WRB, 2007) and the Soil Taxonomy (Soil Survey Staff, 2010)), although in some horizons rather low values were measured in the topsoil (Table 2). In several soils another important criteria (Al_o + 1/2Fe_o > 2% within the first 25 cm) did not meet the andic requirements (data not shown; Egli et al., 2007). Nonetheless, the soils can be classified as Andosols as this Reference Soil Group of the WRB classification can have either a vitric or an andic horizon starting less than 25 cm below the soil surface. The requirements for vitric properties were fulfilled in all soils. Furthermore, additional criteria that are used to describe andic properties met the requirements such as an organic C content of less than 250 g/kg in all soil horizons or more than 30% of the fine earth fraction having a particle size > 20 µm. In general, the soils were variations of Vitric Andosols (WRB) or Typic Haploxerand to Typic or Humic Hapludand (according to the Soil Taxonomy). The soils usually have a mollic character (with respect to the colour, org. C content and base saturation) at the lower sites and an umbric one at the highest. The thickness of the topsoil, however, does not fully meet the requirements for a mollic or umbric horizon (except for the soil at 1090 m asl).

The soils were weakly acid and most of them did not show an evident pH gradient within the profile. The pH values of genetic horizons along with total C and N and C/N ratios are reported in Table 3. The total content of the fine earth of one replicate per site is given in Table 4. The chemical composition along and between the soil profiles varies only slightly. Some minor discontinuities along the profiles might be either due to occasional ash input or to weathering (leaching). In general, the soil material can be considered as quite homogeneous and fully fits the expectances for the chemistry of eruptive rocks and ashes of the Mongibello chronozone or the ancient Mongibello chronozone (Pichler, 1984).

Soil organic matter

The mean concentration of organic matter shows a decreasing trend with increasing altitude for both the soil depth intervals 0 – 15 and 15 – 40 cm (Table 5). The variability is however relatively high.

With increasing altitude, precipitation increases and temperature decreases (Table 1). According to this observed trend, in such an environment higher temperature leads to an increase of SOC (soil organic carbon) and higher precipitation to a decrease. The C/N ratio changes abruptly between 1090 and 1515 m asl most probably because of to the transition from maquis vegetation, oak and chestnut forests to coniferous stands. The high C/N variability at an altitude of 1515 m asl is predominantly due to an outlier (C/N of 87): without this outlier, the C/N ratio at 1515 and 1772 m asl would be rather similar.

Carbon recovery after oxidation by H_2O_2 was usually between 13 and 30% (range: 1 – 50 %). The recoveries did not change with increasing soil depth which is rather unusual (Table 6; cf. Egli et al., 2009). A similar behaviour could be measured for nitrogen. Nitrogen recovery was usually between 12 and 33% (range: < 1 – 44%). Also with N, the recoveries did not change with increasing soil depth. Compared to the untreated soils, the H_2O_2 treatment would be expected to lead to a relative enrichment of nitrogen (lower C/N ratios after the treatment; see Favilli et al., 2008; Egli et al., 2009). This was, if ever, only partially the case. In topsoil horizons (0 – 40 cm soil depth) such a trend was detectable, not so in the subsoil. Although only one soil profile per site was investigated regarding the distribution of labile and stable organic matter, which consequently provides a small database, a trend of an increasing proportion of labile SOM with decreasing altitude seems to exist for both considered depth intervals (0 – 15 and 15 – 40 cm). These trends have, however, an error probability of > 5%. In 0 – 15 cm soil depth and, less pronounced, in 15 – 40 cm, the proportion of the labile carbon and nitrogen increased with decreasing altitude (Fig. 2). The altitudinal trends for labile N had an error probability of < 5%.

The range of the $\partial^{13}C$ values (Table 7) is typical for C3 plants (Mook and Waterbolk, 1985). A trend ($p < 0.05$) towards lower $\partial^{13}C$ values (and consequently a SOM fraction that is more depleted in ^{13}C) at 0 – 15 and 15 – 40 cm soil depth with increasing altitude can be observed (Fig. 3).

Radiocarbon age of the stable SOM fraction

The ages of the stable organic matter fraction varied considerably: from modern ages up to more than 8 ky old carbon fractions were detectable (Table 7). In some soils an increase in age of the stable SOM with depth was found, while at 1772 m asl the highest age was measured in the surface horizon. At several sites, a modern age of the stable SOM fraction was measured in the surface horizon. Either H_2O_2 was unable to oxidise all young OM in these horizons or almost no old carbon exists in these horizons. However, since the H_2O_2 method usually works fine for soils having an organic C content of ≤ 110 g/kg (Favilli et al., 2008), we assume that in several surface horizons almost all the old OM had been replaced by younger OM.

Rather young ages of the resilient organic fraction were measured in the top- and subsoils at low altitudes.

The measured age in the subsoil of the site 1515 m asl is 8 ky BP and quite close to the age of the soil (also around 8 ky BP). Some of the pristine organic matter evidently still exists in this soil. In the topsoil, the input of fresh organic matter is high and probably replaced all old OM. Also at the site with the highest elevation (1772 m asl), very old ages of stable organic matter were measured (around 6.5 ky BP). At all other sites, the maximum age of the stable organic matter was in the range of 1.1 – 1.6 ky BP.

These findings support that the elevation – via lower temperatures in the biologically active period, which limit SOM decomposition – and fire activity, which indiscriminately removes all organics from the ground, must have an important impact on the turnover rate of the stable organic matter fraction.

Charcoal

The age of the charcoal pieces varied from 0 to about 1.6 ky BP (Table 8). At the lowest site, almost all of the charcoal had a modern age. Only one piece at a depth of 55 – 65 cm was slightly older. The charcoal composition at this site reflects reasonably well the maquis vegetation. Also at 866 m asl, the present-day vegetation (maquis) is predominantly reflected in the charcoal composition. *Castanea sativa* is actually not present but apparently grew here a few hundred years ago. Also here, only rather young ages could be measured. At 1090 m asl, charcoal pieces having an age of several centuries could be found (Table 8).

At the highest site (1772 m asl), increasing ages of charcoal were measured with increasing soil depth. Nonetheless some age inversions could be detected along the profile which is often typical in soils. It usually indicates the downward migration of charcoal pieces, which is plausible in coarse-textured soils like those investigated. Highest ages were recorded at a depth of 55 – 65 cm with ages in the range of about 1 – 1.6 ky BP. At this site, only charcoal pieces deriving from *Pinus nigra* could be identified. This shows that the vegetation has not changed over the last 1.6 ky. Some *Fagus sylvatica* charcoal could be related to the age < 300 y BP. *Fagus sylvatica* is not uncommon in these areas. Nowadays, it usually grows at altitudes > 1500 m asl. Some individual examples of this species occurred at the highest site.

Discussion

Charcoal and charred organic material is present in substantial amounts in the investigated soils. In fact, up to almost 40% of the organic carbon concentration can be charcoal (Table 5). There is evidence that charred organic carbon plays an important role in storing carbon in many soils worldwide such as Chernozems in Russia (e.g. Schmidt et al., 1999), Hapludolls in Argentina (Zech et al., 1997), volcanic ash soils in Japan (Golchin et al., 1997) or in soils of the French Alps (Carcaillet and Talon, 2001). The frequent burning of vegetation produces black carbon that contributes to highly stable organic matter in soils (Schmidt and Noack, 2000). Soil carbon sequestration in the form of charcoal is hence significant in biomes having a dry climate (or periods of dry conditions) and fire-prone vegetation (Carcaillet and Talon, 2001; Rovira et al., 2009).

In general, the stability of depolymerised and microbially-transformed detritus is thought to depend on intrinsic soil properties such as surface chemistry (Kleber et al., 2007). Organic fractions having slow turnover rates are mostly found when associated with soil minerals, except for fire-derived organic matter (Marschner et al., 2008). The presence of free particulate charcoal (not bound to the mineral phase) and its significant correlation to org. C is an evidence that not only sorption to mineral surfaces but also molecular recalcitrance is an important factor (Eckmeier et al., 2010).

Although the climate, fire and vegetation interactions are complex in the considered system, fire activity has most probably influenced several important soil processes in the Etna region (Egli et al., 2007). Soil organic carbon (SOC) and especially soil organic nitrogen (SON) seem to accumulate at lower altitudes, because of both specific climatic conditions – a more pronounced change in periods of humidity alternating with periods of droughts – and a higher fire activity. The positive correlations between altitude and SOC or SON content or stock (Figs 2 and 4) support such a hypothesis.

Furthermore, fire activity (and indirectly also climate) seems to have an impact on the distribution of labile and stable organic matter as well as on the age of the stable organic matter fraction (Figs 2 and 5). With increasing fire intensity (and warmer climate), more labile organic matter is accumulated in the soils and the age of the stable fraction decreases. Consequently, the soils at a lower altitude have a higher amount of labile organic matter. Although no systematic datasets about fire distribution and frequency exist in the investigated region, practical experience of the forestry service supports that in general a higher fire frequency is observed in forests at lower altitudes (especially at altitudes < 1000 m asl). According to González-Pérez et al. (2004), the main transformations exerted by fire on soil humus is the accumulation of new particulate C forms 'highly resistant to oxidation and biological degradation' including the so-called 'black carbon'. Our results do not fully match to this statement. In the investigated soils of the Etna, the fire-affected soil organic matter can be ascribed rather to the labile and, therefore, more easily degradable fraction. The accumulation of this labile fraction at lower altitudes is probably also due to fire damage to the soil biota (and the subsequent lower biodegradation of organic matter, Bárcenas-Moreno and Bååth, 2009) or to the reduced biological activity induced by the aridity of soils during the summer months. According to Knicker (2007), char is a heterogeneous mixture of heat-altered bio-polymers having domains of relatively small polyaromatic clusters, but considerable substitution with N, O and S functional groups. Such a concept implies fast oxidation facilitating both microbial attack and dissolution.

In general, a higher org. C (and N) abundance can be measured at lower altitudes of our gradient (Fig. 4) although the trend for C is only significant only at a p-level of around 0.1, for both the whole soil profile and the depth interval 0-40 cm. The correlation between altitude and nitrogen is, however, more stringent. The increase in org. C with decreasing altitude can be at partially attributed to fire activity as there is a significant correlation between the C and charcoal stocks (Fig. 6). A similar tendency is also observed in the dry French Alps where at high elevations, the soil carbon derived from charcoal is negligible whereas at low altitudes (and a consequently warmer climate) the contribution of the charcoal to SOC is considerable (Carcaillet and Talon, 2001). As expected, no significant correlation exists between N stored in the charcoal fraction and the N stocks in the soils. Nitrogen is fixed in a labile fraction that most probably has been chemically altered due to fire effects (black carbon?). The chemical nature of the labile fraction was however not determined.

Increased fire activity at lower altitudes seems to prevent a longer stabilisation of soil organic matter (charcoal included). The age-trend of the stable organic matter with the altitude shows that this fraction is not so very quickly removed (due to burning processes) at high altitudes (Fig. 5), while fire appears to negatively affect the stable SOM turnover rate at lower altitudes where finally fires are more frequent. The young ages could of the stable SOM at low altitudes is due to mass movements (erosion) or, more likely, to fire events that prevent the formation of a very old and stable organic matter fraction. Due to the well-preserved soil profiles and the topography, erosion processes seem to be of minor importance. Major discontinuities in the soil profile are, thus, unlikely. Interaction mechanisms between OM and the mineral matrix also play a role in SOM stabilisation. According to the results of Egli et al. (2007), mineral properties at lower altitudes would be even more favourable to fix stable organic matter (due to the higher amount of kaolinite, imogolite-type material and oxyhydroxides). Consequently, fire activity must have an important impact on the turnover rate of the stable organic matter fraction. Our findings suggest that the high fire frequency is a powerful rejuvenating factor for soil organic matter, removing part of the very old, biologically recalcitrant SOM. The differing vegetation, which is due to the changing climatic and other conditions along the toposequence, also contribute to the observed trend. Our results suggest that the stable SOM reflects a climate signal (with a lower turnover rate at higher elevated sites). As already demonstrated by Tewskbury and Van Miegroet (2007), cooler climatic conditions may lead to a longer residence time of OM in soils. Climate- (and often strongly temperature-) dependent stabilisation of the 'stable' organic matter is, however, controversially discussed in literature (von Lützow and Kögel-Knabner, 2009). Some authors claim that the decomposition rate of the stable OM is not temperature-dependent (e.g. Fang et al., 2005), while according to others (e.g. Melillo et al., 2002), that of labile OM is very temperature-sensitive. Another opinion is that stable OM has even a higher temperature-dependency than labile OM (e.g. Conant et al., 2008; Rey et al., 2008). Furthermore, a fourth group has shown that labile and resistant SOM pools respond similarly to changes in temperature (e.g. Conen et al., 2006). In our studied gradient, most probably several processes (reduced fire activity, cooler climate, changed vegetation) contributed to the higher age of the stable organic matter fraction at higher-elevated sites of Etna. It would seem that none of the contributions made by the individual factors can be fully ruled out.

Additionally, $\partial^{13}C$ values of the stable organic matter fraction show a nice inverse correlation with altitude (Fig. 3). ^{13}C is a useful tracer for studying the contribution of plant types to the C budget, the decomposition and incorporation of organic material into more stable SOM (Andreux et al., 1989; Desjardins et al., 1994; Garcia-Olivia et al., 1994; Golchin et al., 1995; Lichter et al., 2008). This trend is primarily due to the changing vegetation and thus the changing litter input into soils but is probably also influenced by the climate (or a combination of both factors). At lower sites, the contribution of C derived from grass (maybe also from some C4 plants) and shrubs is, due to the vegetation type, most probably higher. Also, during decomposition processes some different isotopic fractionation might have occurred at different altitudes, due to the preference accorded by heterotrophic microorganisms to ^{12}C with respect to the heavier ^{13}C (Balesdent et al. 1993; Ågren et al. 1996). Furthermore, Eilmann et al. (2010) showed that maximum $\partial^{13}C$ values were measured after the hottest and driest period of the year in tree rings, and were associated with decreasing growth rates of trees (Scots pine). After biodegradation of the plant residues, we assume that such an influence should also be detectable in the soil organic matter. The $\partial^{13}C$ in early- and late-wood and after biodegradation also in the SOM reflects climatic conditions (Eilmann et al., 2010) and may indicate that moister conditions in soils exist at higher-elevated sites. Furthermore, a higher fire frequency at the lower sites is hypothesised to lead to a depletion of ^{12}C (and to consequently less negative $\partial^{13}C$ values). This would fit observations made by Shrestha (2009) in subalpine soils of Australia: The C and N of soil organic matter were significantly enriched in ^{15}N and ^{13}C isotopes after fire and had not returned to the pre-fire levels five years after the fire. Other authors, however, did not find any significant fire-induced change in $\partial^{13}C$ in burnt areas (*e.g.* Alexis et al., 2010; Certini et al., 2011).

Some detected trends (e.g. $\partial^{13}C$ or the mean age of the stable organic matter) might to be due to an uneven data distribution. This is not very surprising, as some distinct changes in the soil are due to a change in vegetation. Nonetheless, several gradual changes and strict relationships could be found (Figs. 2 and 4) that are either due to climatic conditions or the fire regime. Most of the data had, furthermore, a normal distribution (which would indicate homoscedasticity of the datasets; Table 9). The $\partial^{13}C$ values, however, do not show a normal distribution. The presence of two different datasets is under such circumstances more likely (see above): in this case, the higher sites (having *Pinus nigra*) can be distinguished clearly from the lower sites.

The factors fire, climate and vegetation are interrelated. Consequently, a clear subdivision is not always possible. The increase of labile C and N with decreasing altitude (Fig. 2), the decreasing age of the stable OM with decreasing altitude (Fig. 5), the relationship between the charcoal C and org. C abundance (Fig. 6) and the lack of old charcoal fragments (due to continuous removal by fire; Fig. 7; see below) at lower altitudes are explicit signs of an increasing influence of fire on soils with decreasing altitude.

The charcoal composition primarily reflects the three different vegetation systems: maquis at low to mid, chestnut and oak forests (Supra-Mediterranean zone) at mid and pine at high elevations. Preconditions for forest fires are the presence of a substantial amount of flammable trees and litter, a relatively dry climate or periods with drought and thunderstorms (lightning). Another natural factor promoting wildfires in the studied area is the incandescent material erupted by the volcano, as both lava flows and ejecta. Furthermore, human activity also contributes substantially to the incidence of fires in the Mediterranean basin (Pausas et al., 2008; Novara et al., 2010). Similar to findings in the Alps (e.g. Favilli et al., 2010), and as inferred by the identification and dating of charcoal fragments (Fig. 7), vegetation at highly-elevated sites on Etna has not changed much during the last centuries to millennia. At low altitudes, the fire frequency seems to be too high to enable preservation of old charcoal particles; here, a reconstruction of the vegetation history was thus hardly possible. Several traced fire events occurred in fact in the Modern Period. At sites > 800m asl, a reconstruction of the vegetation back to the Middle Ages was possible. At the highest altitude, fires that occurred at the end of the Roman period were detectable. This may well reflect a climatic signal of fires, with frequent burning at the lower sites that is accompanied by a continuous removal of older charcoal, but probably also points to the intensity of human impact at lowest altitudes. As shown by Gates and Liess (2001), Hughes (2010) and Henry et al. (2010), human impact has been a determining factor in the evolution of the Mediterranean landscape – in some parts since the Neolithic and Bronze age. Although climate change will alter vegetation composition, future dynamics of mountain forests and soils will be co-determined by anthropogenic fire (Colombaroli et al., 2010).

Conclusions

We measured several parameters to investigate the effect of fire on SOM characteristics and to trace back landscape evolution using charcoals. The studied soils have recorded the signals of the interrelated factors fire frequency, climatic effects and vegetation that cannot always be clearly subdivided. Although some of the measured parameters do not have a huge statistical database, they all point into a similar direction. Our results show that fire is a driving factor of landscape evolution and pedogenesis of the Etna region. In particular, it strongly affects the characteristics of soil organic matter:

- Carbon and especially nitrogen stocks seemed to be higher at lower-elevated than at higher-elevated sites (the trend is however significant only with an error probability of > 5%). The accumulation of C correlated with the stocks of charcoal in the soils. The C in charcoal can comprise up to almost 40% of SOC.
- Labile SOM seemed to increase with decreasing altitude (for N this increase was significant whereas for C the error probability was >5%). The increased fire activity with decreasing altitude, the change in vegetation and climate seem to lead to the accumulation of the labile SOM fraction and to the removal of the old and stable one.
- Fire frequency seems to be a powerful rejuvenating factor for soil organic matter. In fact, the age of the stable soil organic matter strongly increased with increasing altitude, so much that in some soils at high altitudes, the stable SOM was close to the age of the soil.
- Natural and human-induced fires have repeatedly affected the landscape evolution. The identification and dating of charcoal pieces reveal that more frequent fires must have occurred at the lowest altitudes. At high altitudes, where a longer charcoal time-sequence was available, the general type of vegetation has not changed greatly over the last centuries to millennia.

The soils have recorded the signal of fire frequency, vegetation and climatic effects. Vegetation is, however, not a fully independent factor as it is influenced by climate and fire. With decreasing altitude and, therefore, with a warmer climate, fire frequency, SOM abundance and the amount of labile SOM seemed to increase. Although fire strongly determines the fate of several soil aspects, fire frequency and intensity on the surveyed area of Mt Etna are, however, still moderate enough even at the lowest altitudes for the SOM pool to be still high and not depleted.

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Table 1

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Table 1. Characteristics of the study sites in the Etna region.

Elevation (m a.s.l.)	Coordinates	Aspect	Slope (°)	MAT[1)] (°C)	MAP[2)] (mm)	Soil moisture regime	Soil temperature regime	Parent material	Vegetation	Soil type (IUSS Working Group WRB, 2007; Soil Survey Staff, 2010)
551	37.8784° N / 15.0900° E	N	0	15.3	1000	xeric	thermic	Ve-Lava (Trachy-basalt)	Macchia Mediterranea/Quercion ilicis with *Quercus pubescens, Asphodelus microcarpus, Carlina nebrodensis, Artemisia spec., Genista aetnensis, Rubus spec., Dryopteris filix-mas*	Vitric Andosol Typic Haploxerand
866	37.8512° N / 15.07025° E	N	4	13.1	1100	udic	mesic	Ve-Lava (Trachy-basalt)	Macchia Mediterranea/Quercion ilicis with *Quercus ilex, Quercus pubescens Wild*	Vitric Andosol Typic Udivitrand
998	37.8538° N / 15.0027° E	N	3	12.5	1100	udic	mesic	Ve-Lava (Trachy-basalt)	Macchia Mediterranea/Quercion ilicis with *Quercus ilex, Quercus pubescens Wild, Castanea sativa, Genista aetnensis, Rubus spec., Dryopteris filix-mas*	Vitric Andosol Typic Udivitrand
1090	37.8266° N / 15.0831° E	N	0	11.9	1150	udic	mesic	Ve-Lava (Trachy-basalt)	Supra-mediterranean zone - Macchia Mediterranea /Quercion ilicis with *Quercus ilex, Quercus pubescens Wild, Castanea sativa, Genista aetnensis, Daphne laureola L., Orchis commutata, Muscari spec., Rubus spec., Dryopteris filix-mas*	Vitri-Mollic Andosol Humic Udivitrand
1515	37.8097° N /	N	4	9.2	1250	udic	mesic	Ve-Lava	Coniferous forest (*Pinus nigra ssp.*	Vitric Andosol

	15.0640° E							(Trachy-basalt)	*laricio*) with a few deciduous trees (*Fagus sylvatica, Quercus pubescens, Castanea sativa*)	Vitric Hapludand
1772	37.7915° N / 15.0428° E	N	12	7.5	1400	udic	frigid	Ve-Lava (Trachy-basalt)	Coniferous forest (*Pinus nigra ssp. laricio, Dryopteris filix-mas, Iuniperus sp.*)	Vitric Andosol Typic Udivitrand

[1)]MAT = mean annual temperature (°C), [2)]MAP = mean annual precipitation

Table 2
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Table 2. Some physical characteristics of the main soil profiles along the toposequence in the Etna region.

Altitude m asl	Soil horizon	Depth (cm)	Munsell color (dry)	bulk density g cm^{-3}	Skeleton Weight-%	Sand g kg^{-1}	Silt g kg^{-1}	Clay g kg^{-1}
551	A1	0-5	5YR 2.5/1	0.45	8.5	476	328	197
	A2	5-15	5YR 2.5/2	1.11	15.3	540	372	88
	Bw	15-65	10YR 3/3	1.40	34.6	699	234	66
	BC	65-85	10YR 4/6	1.37	35.2	827	124	49
866	A	0-15	7.5YR 2/2	1.29	14.0	652	259	89
	Bw	15-40	7.5YR2/2	1.05	15.2	664	261	75
	BC	40-70	7.5YR 3/2	0.78	7.6	462	455	83
998	A1	0-3	7.5 YR 2.5/0	1.05	15.7	625	262	112
	A2	3-20	5YR 2.5/2	1.23	25.5	573	329	98
	Bw	20-70	7.5 YR 5/6	1.64	51.3	769	174	57
	B(C)	70-90	7.5 YR 3/2	1.53	48.1	789	164	47
	C	90-117	7.5 YR 3/2	1.57	52.2	836	117	47
1090	A1	0-6	10YR 3/3	1.01	15.2	673	236	92
	A2	6-25	10YR 3/3	1.09	28.2	656	255	90
	Bw	25-65	5YR 2.5/2	0.75	23.3	429	496	75
	C	65-80		0.60				
1515	A1	0-7	5YR 2.5/1	0.72	14.7	739	148	113
	A2	7-23	10YR 2/2	0.93	15.9	828	106	65
	B1	23-38	5YR 2.5/1	0.84	12.4	812	132	56
	B2	38-98	10YR 3/4	1.00	8.3	732	213	55
	C	98-122		0.71	14.9	723	202	76
1772	A1	0-4	10YR 2/3	0.95	10.0	802	137	61
	A2	4-13	10YR 2/3	1.19	11.0	887	67	46
	AB	13-23	2,5Y 2/4	1.01	8.5	592	342	66
	B	23-100	10YR 6/5	0.78	8.4	791	166	43
	BC	100-140	10YR 6/5	1.04	18.4	666	277	57
	C	140-150	10YR 3/3	1.00	10.0	751	182	67

Table 3

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Table 3. Organic carbon, nitrogen, C/N ratios and pH-values of the main soil profiles along the toposequence in the Etna region.

Altitude m asl	Horizon	pH ($CaCl_2$)	total C g kg^{-1}	total N g kg^{-1}	C/N
551	A1	6.30	132.6	10.79	12.3
	A2	5.90	52.6	4.19	12.6
	Bw	5.65	30.7	2.75	11.2
	BC	5.35	10.0	0.85	11.8
866	A	5.95	35.1	2.47	14.2
	Bw	6.35	29.6	2.24	13.2
	B	6.10	49.8	4.60	10.8
998	A1	6.20	90.3	7.68	11.8
	A2	5.65	54.5	4.98	10.9
	Bw	5.50	10.4	0.91	11.4
	BC	5.60	5.7	0.51	11.2
	C	5.70	5.1	0.51	10.0
1090	A1	5.70	45.6	3.54	12.9
	A2	5.45	26.2	2.16	12.1
	Bw	5.15	45.3	4.70	9.6
	C	5.55	8.2	0.71	11.5
1515	A1	5.05	65.2	2.3	28.3
	A2	5.20	22.5	0.79	28.5
	B1	5.50	22.2	0.87	25.6
	B2	5.60	12.7	0.67	19.0
	C	5.55	11.3	0.61	18.5
1772	A1	4.90	24.8	1.02	24.3
	A2	5.00	10.7	0.41	26.0
	AB	5.35	13.2	0.67	19.8

	B	5.70	6.6	0.42	15.8
	BC	5.70	13.8	0.72	19.2
	C	5.80	7.0	0.44	15.9

Table 4
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Table 4. Total content (referred to the organic-free fraction) of major and the most relevant minor components in the fine earth of the soils along the toposequence (one soil profile per site).

Altitude m asl	Soil depth cm	Na_2O %	MgO %	K_2O %	CaO %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	P_2O_5 %	MnO %	V_2O_5 %	SrO %	ZrO_2 %
551	0-15	1.57	1.69	1.38	5.77	50.25	18.41	9.10	1.92	0.851	0.175	0.031	0.109	0.036
	15-40	1.41	1.47	1.20	4.98	46.76	18.47	8.87	1.87	0.789	0.171	0.033	0.103	0.036
	40-55	2.38	1.94	1.53	6.32	51.52	20.04	9.41	1.96	0.776	0.176	0.039	0.121	0.038
	55-85	3.20	2.07	2.07	7.24	52.63	17.87	9.04	1.93	0.822	0.176	0.021	0.138	0.037
866	0-15	1.89	2.45	1.47	7.54	50.73	16.22	10.28	2.07	0.816	0.182	0.042	0.136	0.033
	15-40	1.86	2.36	1.54	7.21	48.51	15.27	10.19	2.14	0.796	0.178	0.036	0.135	0.034
	40-70	1.46	1.93	1.15	6.41	52.74	18.54	9.41	1.93	0.717	0.179	0.041	0.136	0.033
998	0-15	1.98	2.38	1.39	7.88	54.02	17.82	9.96	2.13	0.811	0.177	0.043	0.156	0.033
	15-40	1.93	2.12	1.24	7.07	49.67	16.79	9.11	1.96	0.693	0.161	0.039	0.145	0.029
	40-90	2.56	2.56	1.74	8.44	49.53	14.44	10.30	2.16	0.926	0.178	0.029	0.156	0.035
1090	0-15	2.12	2.25	1.28	7.28	50.31	16.57	9.40	1.96	0.658	0.169	0.047	0.135	0.032
	15-40	1.43	1.65	1.09	5.65	47.11	15.03	8.85	1.89	0.585	0.163	0.038	0.124	0.033
	40-70	2.74	2.11	1.46	6.33	53.31	18.96	9.18	2.11	0.895	0.187	0.034	0.148	0.040
1515	0-15	2.48	2.42	1.50	8.85	52.17	15.88	9.58	1.92	0.571	0.174	0.045	0.138	0.032
	15-40	2.78	2.49	1.51	9.50	53.71	17.38	9.70	1.99	0.586	0.165	0.047	0.154	0.032
	40-55	1.93	1.83	1.19	5.74	50.18	20.24	9.78	2.13	0.734	0.173	0.044	0.134	0.037
1772	0-15	2.08	2.24	1.56	8.00	49.34	12.88	9.42	1.91	0.496	0.160	0.051	0.129	0.030
	15-40	3.08	2.86	1.56	9.68	53.12	16.66	9.81	1.95	0.538	0.166	0.049	0.144	0.032
	40-55	2.32	2.31	1.46	7.43	52.28	18.85	9.78	2.04	0.721	0.159	0.045	0.131	0.036
	55-70	1.80	2.03	1.18	6.19	52.09	20.44	10.07	2.12	0.718	0.176	0.044	0.134	0.033
	70-80	2.31	3.48	1.30	10.34	50.76	14.08	10.43	1.88	0.463	0.176	0.044	0.127	0.027
	mean	2.16	2.22	1.42	7.33	50.99	17.18	9.60	2.00	0.713	0.172	0.040	0.135	0.034
	SD	0.52	0.44	0.23	1.43	2.05	2.09	0.48	0.10	0.131	0.008	0.007	0.014	0.003

Table 5
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Table 5. Some physical properties, C, N and charcoal (as amount of charcoal and C stored in charcoal) of the inventory sites along the toposequence.

Altitude m asl	Soil depth cm	Soil skeleton weight-%	Density g/cm^3	Ctot g/kg	N g/kg	C/N	Charcoal g/kg	Charcoal C g/kg	Charcoal C/Ctot %
551	0 - 15	40.3 (±18.3)	0.87 (±0.38)	64.2 (±27.3)	5.05 (±2.38)	13.0 (±0.9)	3.35 (±2.92)	2.40 (±2.09)	3.7
	15 - 40	47.2 (±31.4)	0.94 (±0.37)	44.1 (±7.6)	3.42 (±0.71)	12.9 (±0.5)	0.00 (±0.00)	0.00 (±0.00)	0.0
866	0 - 15	14.0 (±3.7)	1.13 (±0.18)	43.4 (±24.2)	2.88 (±1.42)	14.8 (±0.9)	5.11 (±5.40)	3.38 (±3.57)	7.8
	15 - 40	15.2 (±1.7)	1.08 (±0.03)	40.7 (±15.7)	2.67 (±0.45)	14.9 (±3.3)	20.89 (±17.33)	13.52 (±11.21)	33.2
998	0 - 15	50.1 (±8.7)	1.02 (±0.13)	64.9 (±7.7)	5.86 (±0.45)	11.1 (±1.3)	0.88 (±1.52)	0.54 (±0.94)	0.8
	15 - 40	70.6 (±4.3)	1.52 (±0.07)	14.6 (±3.4)	0.90 (±0.37)	16.9 (±2.8)	0.00 (±0.00)	0.00 (±0.00)	0.0
1090	0 - 15	22.4 (±4.4)	1.01 (±0.05)	33.6 (±5.0)	2.48 (±0.44)	16.9 (±2.5)	2.68 (±2.33)	1.34 (±1.16)	4.0
	15 - 40	24.3 (±1.6)	0.90 (±0.10)	32.1 (±5.0)	2.40 (±0.31)	12.1 (±1.9)	3.11 (±5.38)	1.53 (±2.65)	4.8
1515	0 - 15	6.0 (±4.0)	0.89 (±0.13)	27.6 (±9.7)	0.90 (±0.62)	46.8 (±35.3)	4.34 (±3.95)	2.58 (±2.35)	9.3
	15 - 40	3.7 (±2.4)	1.06 (±0.06)	33.5 (±13.7)	0.93 (±0.23)	35.2 (±5.8)	19.52 (±15.86)	12.16 (±9.88)	36.3
1772	0 - 15	10.2 (±2.0)	0.97 (±0.15)	37.3 (±11.8)	1.46 (±0.81)	28.6 (±7.4)	1.10 (±2.19)	0.77 (±1.54)	2.1
	15 - 40	14.0 (±14.1)	1.09 (±0.10)	11.4 (±4.5)	0.32 (±0.16)	37.9 (±5.5)	1.78 (±2.06)	1.11 (±1.28)	9.7

Table 6
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Table 6. Stable and labile C and N fractions in the soils along the toposequence (one soil profile per site).

Altitude m asl	Soil depth cm	Ctot g/kg	Ntot g/kg	C stable g/kg	C labile g/kg	N stable g/kg	N labile g/kg	C/N tot	C/N stable	C/N labile	C recovery %	N recovery %
551	0 - 15	73.0	5.62	13.0	60.0	1.18	4.44	13.0	11.1	13.5	17.8	21.0
	15 - 40	38.7	2.92	5.0	33.7	0.82	2.10	13.3	6.1	16.1	12.9	28.1
	40 - 55	34.3	2.55	6.5	27.8	0.20	2.35	13.4	32.0	11.8	18.9	7.8
	55 - 85	6.6	0.6	1.8	4.8	<0.05	0.60	11.0	-	8.1	27.3	-
866	0-15	35.1	2.47	10.4	24.6	0.77	1.70	14.2	13.6	14.5	29.6	31.2
	15-40	29.6	2.24	3.9	25.7	0.27	1.97	13.2	14.6	13.0	13.2	12.1
	40-70	49.8	4.6	3.3	46.5	0.24	4.36	10.8	13.6	10.7	6.6	5.2
998	0-15	64.3	5.36	9.5	54.9	1.69	3.67	12.0	5.6	14.9	14.8	31.5
	15-40	13.4	0.77	4.0	9.4	0.25	0.52	17.4	15.9	18.1	29.9	32.5
	40-90	9.7	0.31	0.1	9.6	<0.05	0.31	31.2	-	30.8	1.0	-
1090	0-15	31.2	1.99	6.8	24.4	0.62	1.37	15.7	10.9	17.9	21.8	31.2
	15-40	37.4	2.65	5.1	32.3	1.16	1.49	14.1	4.4	21.6	13.6	43.8
	40-70	23.9	1.46	3.9	19.9	0.23	1.23	16.4	17.3	16.2	16.3	15.7
1515	0-15	31.4	1.34	8.0	23.4	0.33	1.01	23.4	23.9	23.2	25.5	24.6
	15-40	27.0	0.87	4.2	22.8	0.17	0.70	31.0	24.7	32.6	15.6	19.5
	40-55	16.6	0.19	4.6	23.6	0.08	1.06	87.5	55.9	22.4	27.7	42.1
1772	0 - 15	22.0	0.58	11.0	11.1	0.24	0.34	38.0	46.4	32.2	50.0	41.4
	15 - 40	14.0	0.45	0.9	13.2	< 0.05	0.45	31.2	-	29.2	6.4	-
	40 - 55	15.5	0.59	2.3	13.2	0.07	0.52	26.3	34.3	25.2	14.8	11.9
	55 - 70	31.7	1.32	8.1	23.6	0.23	1.09	24.0	35.6	21.6	25.6	17.4
	70 - 80	3.2	< 0.05	1.7	1.5	< 0.05	< 0.05	-	-	-	53.1	-

Table 7
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Table 7. Age of the stable organic matter fraction in the soils of the toposequence.

Altitude m asl	Soil depth cm	C-14 age yBP (±SD)	$\partial^{13}C$ ‰	Calibrated age[1)] cal yBP
551	0-15	modern	-19.3 (±1.1)	modern
	15-40	50 (±30)	-19.0 (±1.1)	31–257
	40-55	1605 (±35)	-23.9 (±1.1)	1405–1565
866	0-15	560 (±30)	-17.4 (±1.1)	521–644
	15-40	1315 (±30)	-19.8 (±1.1)	1179–1296
998	0-15	520 (±30)	-19.6 (±1.1)	507–626
	15-40	655 (±30)	-20.1 (±1.1)	556–672
1090	0-15	modern	-21.0 (±1.1)	modern
	15-40	740 (±30)	-18.8 (±1.1)	660–727
	40-70	1605 {±35)	-23.9 (±1.1)	1405–1565
1515	0-15	modern	-22.0 (±1.1)	modern
	15-40	7270 (±35)	-23.2 (±1.1)	8011–8170
1772	0-15	5745 (±35)	-31.4 (±1.1)	6449–6639
	15-40	350 (±30)	-32.0 (±1.1)	315–494
	40-45	1570 (±30)	-25.2 (±1.1)	1385–1535

[1)] 2-σ range

Table 8
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Table 8. Age of some identified charcoal pieces.

Altitude m asl	Soil depth cm	Plant type	C-14 age	$\partial^{13}C$ ‰	Calibrated age[1)] cal yBP
551	0-5	Lonicera	modern	-23.8 (±1.2)	modern
	5-15	Quercus	modern	-23.1 (±1.2)	modern
	5-15	Fagus silvatica	modern	-22.2 (±1.1)	modern
	55-65	Quercus	modern	-24.4 (±1.2)	modern
	55-65	Deciduous shrubs	175 (±50)	-23.1 (±1.2)	0-301
866	15-40	Fagus silvatica	175 (±35)	-23.2 (±1.1)	0-299
	15-40	Quercus	235 (±35)	-19.0 (±1.1)	0-426
	15-40	Castanea sativa	modern	-20.4 (±1.1)	modern
1090	0-15	Quercus	180 (±35)	-21.0 (±1.1)	0-301
	15-40	Castanea sativa	325 (±49)	-23.8 (±1.1)	304-483
1515	15-40	Pinus nigra	100 (±40)	-24.2 (±1.1)	11-270
1772	0-15	Pinus nigra	439 (±45)	-21.0 (±1.2)	324-543
	15-25	Pinus nigra	310 (±45)	-21.0 (±1.2)	290-485
	25-40	Pinus nigra	100 (±40)	-23.2 (±1.1)	11-270
	55-65	Pinus nigra	1600 (±40)	-22.3 (±1.1)	1390-1568
	55-65	Pinus nigra	1170 (±50)	-20.6 (±1.2)	965-1239

[1)] 2-σ range

Table 9
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Table 9. Descriptive statistics of the datasets.

	Mean	Median	Skewness	Normal distribution
C stable (g/kg), 0-40 cm	6.81	5.94	0.22	x
C labile (g/kg), 0-40 cm	27.95	24.53	1.06	x
N stable (g/kg), 0-40 cm	0.63	0.48	0.83	x
N labile (g/kg), 0-40 cm	1.65	1.43	1.23	x
C stable (g/kg), 0-15 cm	9.78	9.96	0.10	x
C labile (g/kg), 0-15 cm	33.06	24.53	0.68	x
N stable (g/kg), 0-15 cm	0.81	0.70	0.822	x
N labile (g/kg), 0-15 cm	2.08	1.53	0.72	x
C stable (g/kg), 15-40 cm	3.84	4.08	-1.82	-
C labile (g/kg), 15-40 cm	22.84	24.25	-0.36	x
N stable (g/kg), 15-40 cm	0.44	0.26	0.99	x
N labile (g/kg), 15-40 cm	1.21	1.10	0.22	x
$\delta^{13}C$, 0-40 cm	-21.97	-19.95	-1.63	-
$\delta^{13}C$, 0-15 cm	-21.78	-20.30	-1.91	-
$\delta^{13}C$, 15-40 cm	-22.15	-19.95	-1.98	-
C stock (kg/m^2)	15.81	15.05	0.95	x
N stock (kg/m^2)	1.10	1.02	0.58	x
Charcoal C (kg/m^2)	1.82	1.27	0.62	x
C stock (kg/m^2), 0-40 cm	9.95	9.92	1.22	x
N stock (kg/m^2), 0-40 cm	0.62	0.57	0.46	x
Charcoal C (kg/m^2), 0-40 cm	1.57	0.60	1.94	-
mean topsoil age (^{14}C)	1573	750	0.91	x

*Normality was checked using the Shapiro-Wilk test: x = normal distribution of the dataset; - = not normal distribution of the dataset.

Figure captions

Fig. 1. Location of the investigation sites (toposequence) in the Etna region (Sicily, southern Italy).

Fig. 2. Organic C and N in the stable and labile fraction along the toposequence (one profile per site) and as a function of soil depth.

Fig. 3. Relationship between $\partial^{13}C$ of the stable fraction of organic matter from 0 – 15 and 15 – 40 cm soil depth and the altitude. The regression curve is given for the depth 0 – 15 cm. For both soil depths, a significant correlation ($p < 0.05$) exists between the altitude and $\partial^{13}C$.

Fig. 4. C and N stocks in the soils along the toposequence. A) shows the values for the whole soil profile (n = 12) and B) the values for the soil depth 0-40 cm (n = 24).

Fig. 5. Mean age (calibrated) of the stable organic matter fraction of the topsoil (0 – 40 cm) as a function of the altitude.

Fig. 6. Correlation between the charcoal and SOC stocks of the individual profiles (one soil profile per site and replicates).

Fig. 7. Composition of the vegetation as a function of time derived from charcoal fragments in the soils. Others = *Lonicera implexa* (551 m asl), Maloideae (866 m asl).

Figure 1
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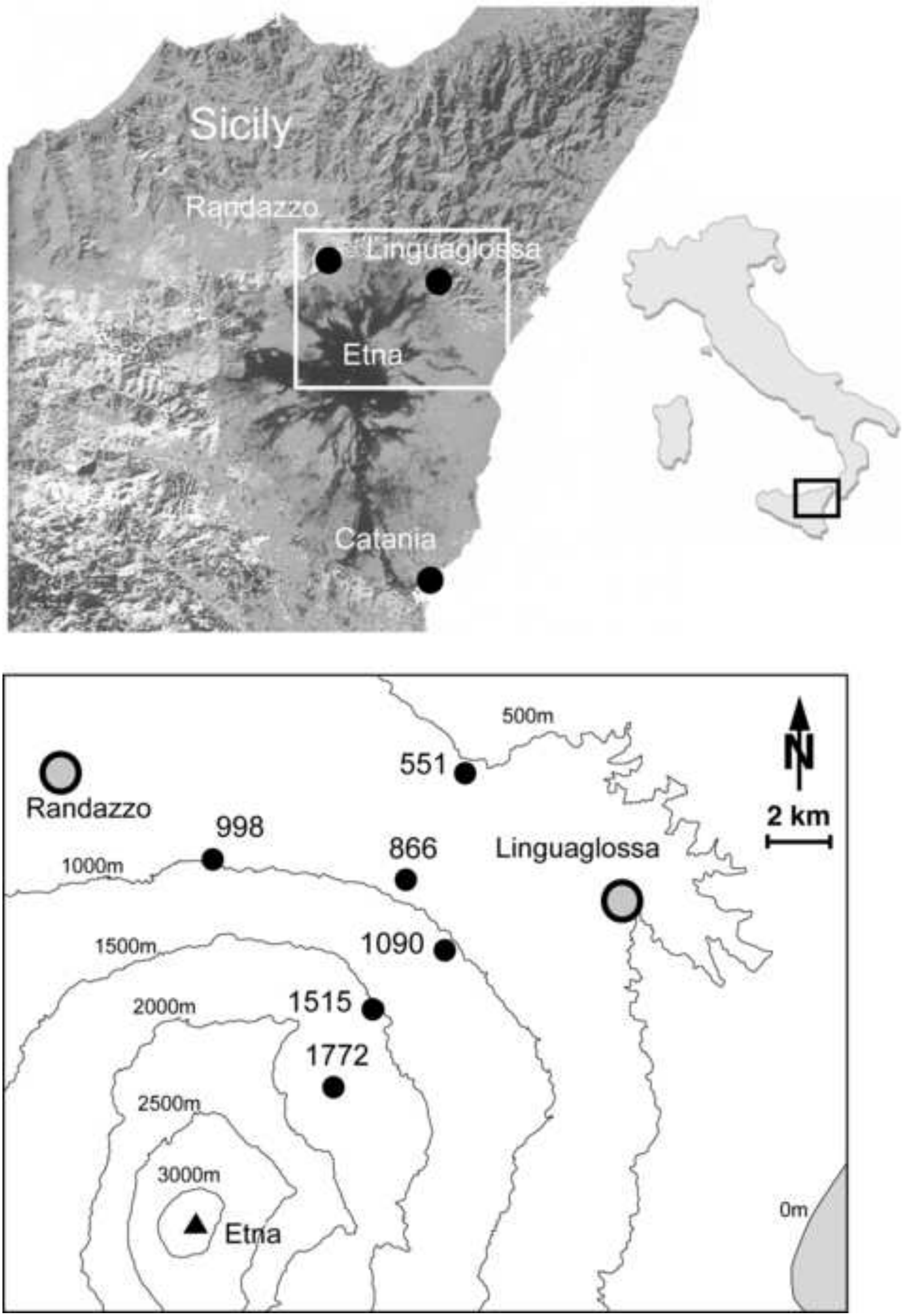

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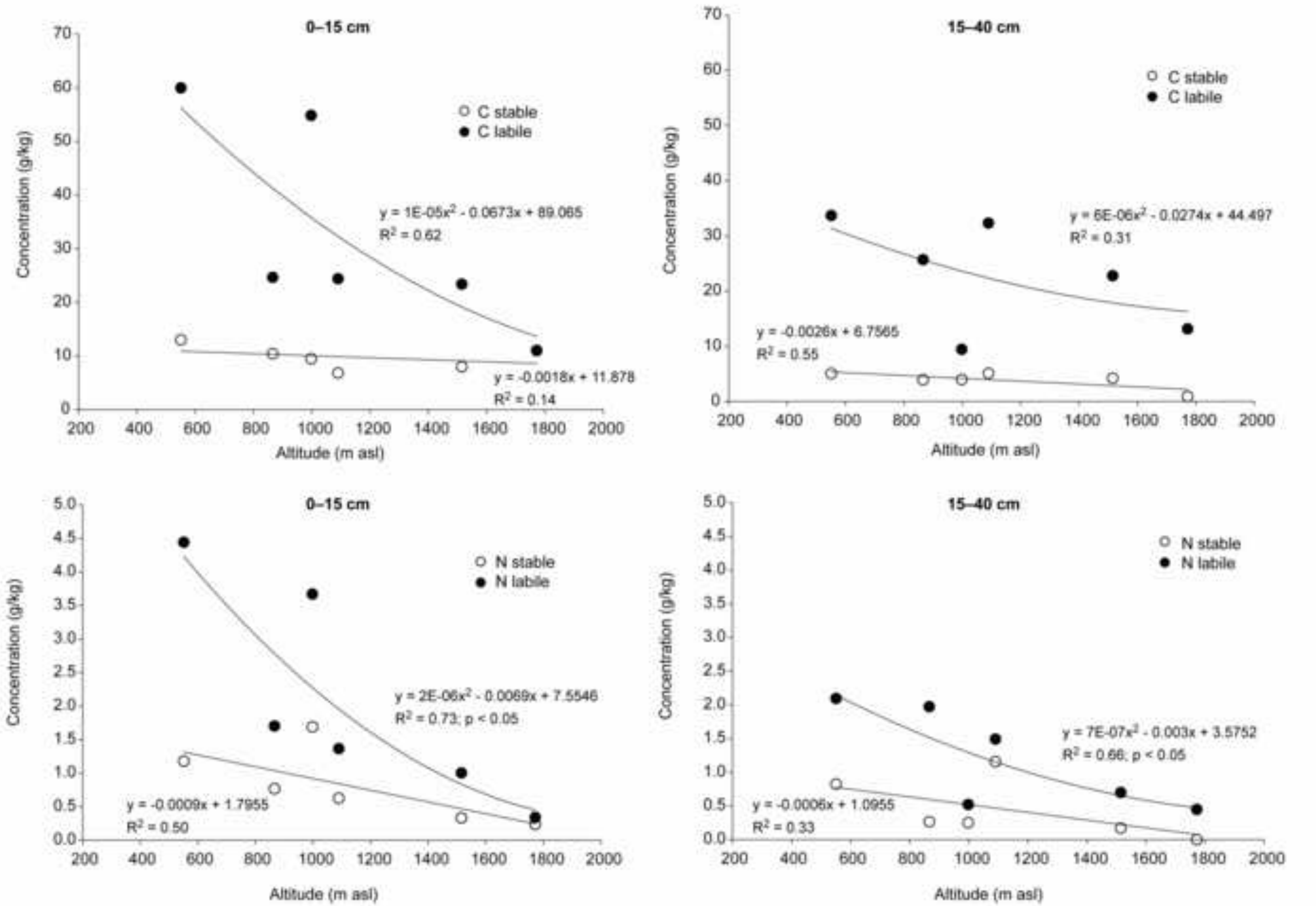

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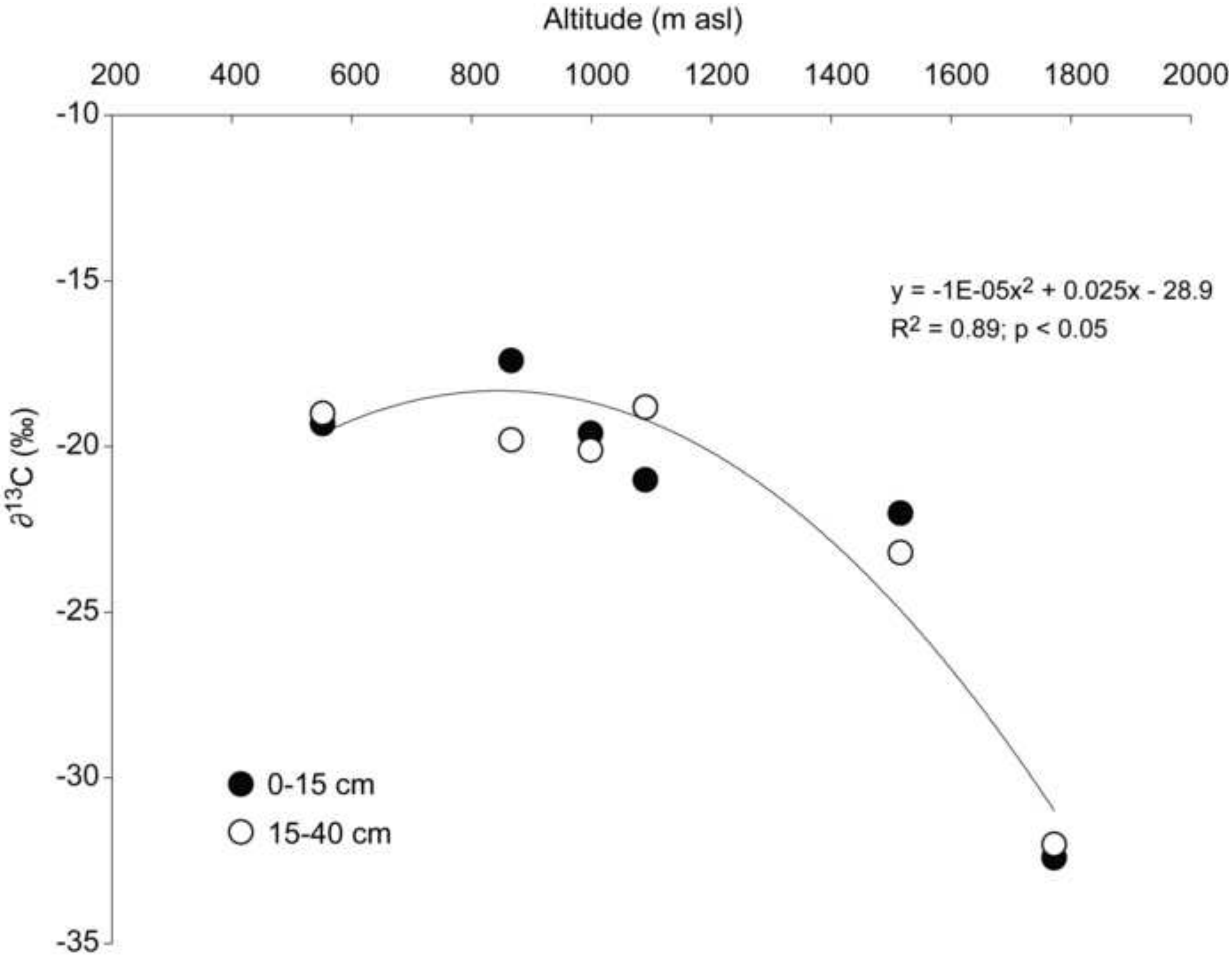

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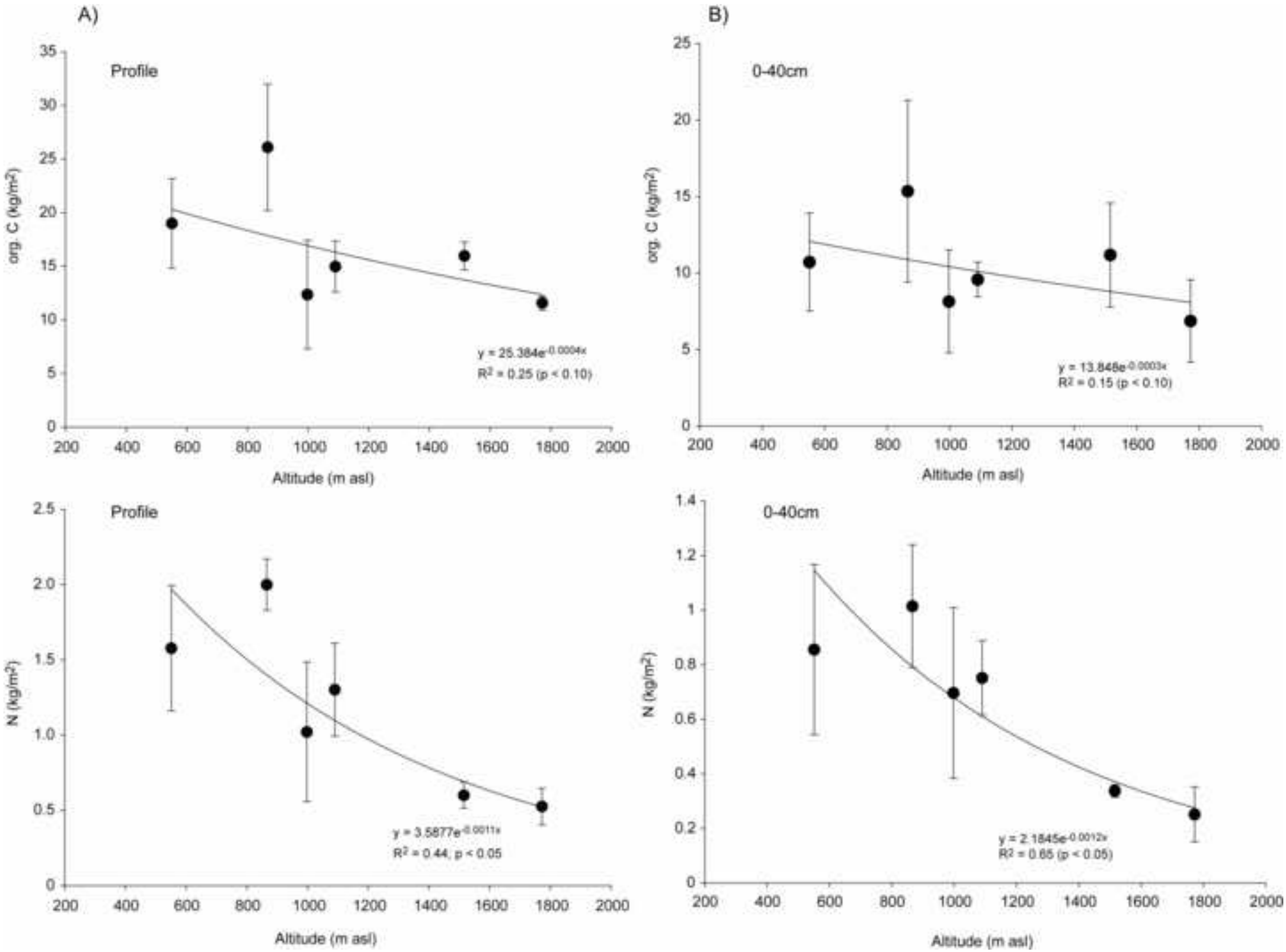

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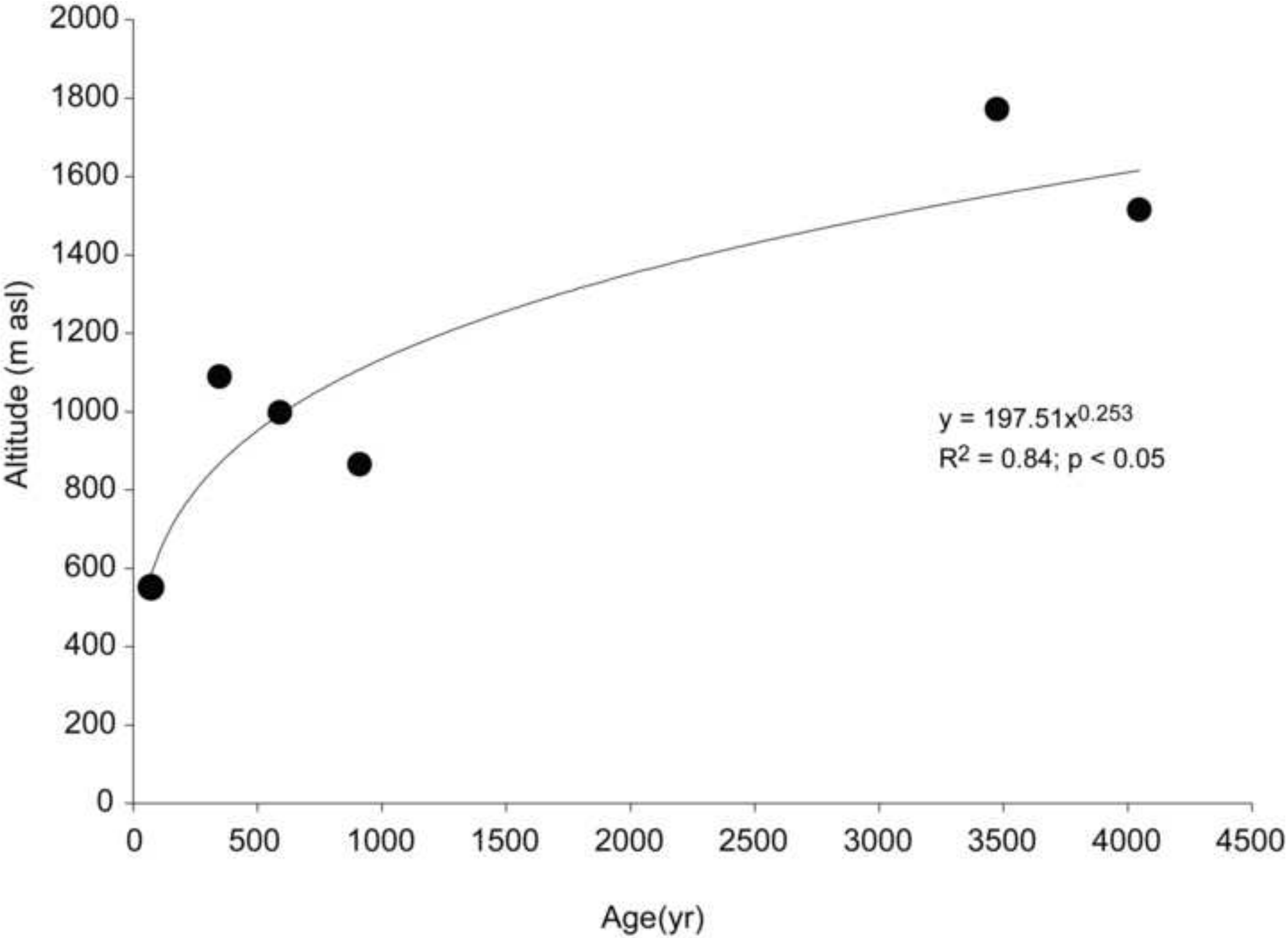

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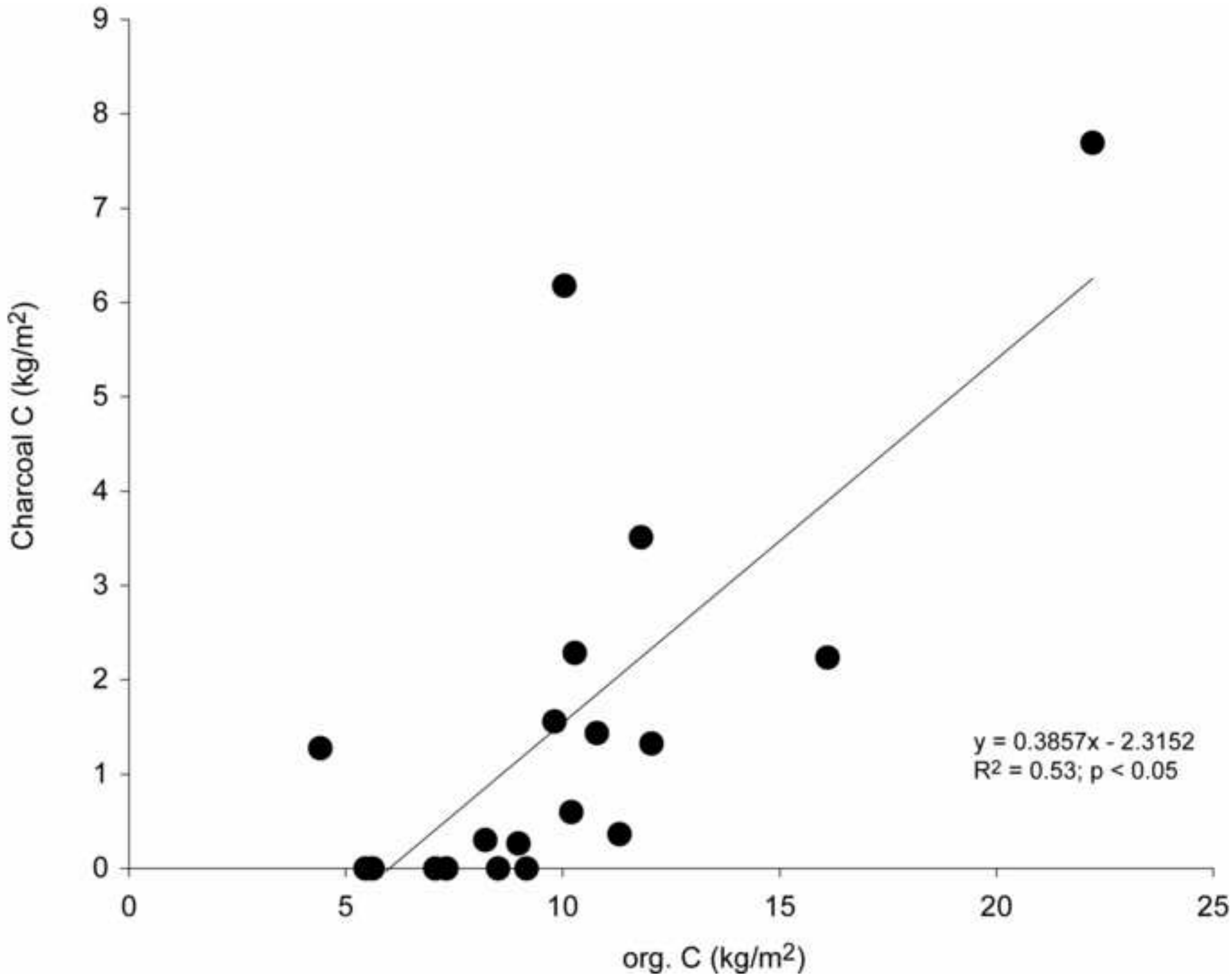

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